

물속에서의 지방족 및 방향족 탄화수소들의 열역학적 성질

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Thermodynamic Properties of Aliphatic and Aromatic Hydrocarbons in Liquid Water

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요약 지방족 및 방향족 탄화수소의 수용액을 Jhon 등이 제창한 liquid water의 significant structure theory를 이용하여 연구하였으며 Helmholtz free energy, internal energy, entropy, heat capacity 등의 열역학적 성질을 계산하였다. 계산결과는 문헌에 발표된 실험치와 잘 일치됨을 볼 수 있다.

Abstract The aqueous solutions of aliphatic and aromatic hydrocarbons have been studied on the basis of the significant structure theory of liquid water proposed by Jhon, et al.

The thermodynamic properties such as Helmholtz free energy, internal energy, entropy, and heat capacity have been calculated.

The results show good agreements with the experiments in the literature.

Introduction

During the past years, several works have been made about the structure of aqueous hydrocarbon solution in order to deduce the thermodynamic properties of hydrophobic bonding.

Nemethy and Scheraga^{1,2} developed the thermodynamic model of the solution based on the Frank and Wen flickering cluster model for water³.

And Hermann⁴ has applied a modified significant structure theory of water to the aqueous

hydrocarbon solution.

Then, the significant structure theory of liquids^{5,6,7} has been successfully applied to the prediction of thermodynamic, dielectric, transport, and surface properties of many liquid systems ranging from simple liquids to complicated systems, such as water and some mixtures.

In this paper, the physical model for the structure of aqueous hydrocarbon solution is developed with the use of domain model for pure liquid water proposed by Jhon, et al.⁸

Theory

Partition Function of Aqueous Hydrocarbon

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Solution In the aqueous hydrocarbon solution, there are hydrocarbon molecules, bulk water molecules, and the adjacent water layer next to the hydrocarbons.

Then, the partition function for the solution of a hydrocarbon in water may be written as follows:

$$Z_{sol} = M Z_R^{N_1} \cdot Z_W^{N_1 - LN_1} \cdot Z_L^{LN_1} \quad (1)$$

$$N_1 + N_2 = N \quad (2)$$

where M is a combinatorial factor, Z_R , Z_W , and Z_L are the partition functions for the hydrocarbon, the bulk water, and adjacent water next to the hydrocarbon, respectively. And L is the numbers of the adjacent water molecules surrounding each hydrocarbon molecule, N is Avogadro's number, N_1 and N_2 are the respective numbers of total water and hydrocarbon molecules.

In this model, the basic assumptions made are that the adjacent water molecule and the remaining bulk water molecule and the remaining bulk water molecule are statistically independent of each other.

Then, the partition function associated with dissolving a hydrocarbon in liquid water is defined as follows:

$$Z_D = \frac{Z_{sol}}{G_R^{N_1} \cdot Z_W^{N_1}} \cdot \frac{1}{M} \quad (3)$$

in which G_R is the partition function for pure hydrocarbon molecule and Z_W is the partition function for pure bulk water.

Substituting equation(1) into equation(3), and after some rearrangement; the following equation is obtained.

$$Z_D = \left(\frac{Z_R}{G_R}\right)^{N_1} \left(\frac{Z_L}{Z_W}\right)^{LN_1} \quad (4)$$

Therefore, the natural logarithm of the above equation(4) is given by

$$\ln Z_D = N_2 \ln \left(\frac{Z_R}{G_R}\right) + LN_2 \ln \left(\frac{Z_L}{Z_W}\right) \quad (5)$$

Using this equation (5), the thermodynamic quantities for the aqueous hydrocarbon solutions can be calculated.

To evaluate the thermodynamic properties such as Helmholtz free energy, internal energy, entropy, and heat capacity, the partition functions for the dissolved hydrocarbon molecule, that of pure hydrocarbon, that of the adjacent water molecule next to the hydrocarbon, and that of pure water molecule must be known.

Partition Function for Hydrocarbons

The partition functions for pure hydrocarbon is written by the significant structure theory as follows:

$$G_R = \left[\frac{e^{E_{ss}/kT}}{(1 - e^{-E_{ss}/kT})^6} \left\{ 1 + n_2 \left(\frac{V_2 - V_2'}{V_2} \right) e^{-\frac{E_{s2}}{(s+1)kT}} \right\} f_{s,rot} \cdot f_{s,vib} \right]^{\left(\frac{V_2}{N_2}\right)} \cdot \left[\left(\frac{2\pi m_2 kT}{h^3} \right)^{\frac{3}{2}} \cdot \frac{eV_2}{N} \cdot f_{s,rot} \cdot f_{s,vib} \right]^{\frac{V_2 - V_2'}{V_2}} \quad (6)$$

Where the first set of brackets represents the solid-like partition function and the second set of brackets is the gas-like partition function.

The subscripts s and g are solid-like and gas-like, and the f_{rot} and f_{vib} are the partition functions for molecular rotation and interatomic vibration, respectively. And θ_2 is the Einstein characteristic temperature, E_{s2} is the sublimation energy, and a_2 and n_2 are the characteristic parameters of hydrocarbon.

On the other hand, the partition function for the dissolved hydrocarbon molecule, Z_R can be similarly formulated. The parameters E'_{ss} , θ'_{2s} , a'_{2s} , and n'_{2s} in Z_R may not practically be the same values as the corresponding parameters in the partition function for pure hydrocarbon molecules, G_R .

However, since the value of n' , a' and θ' are not very much different from those of n , a and θ , it is assumed that corresponding values are treated to be equal. Then, taking the ratio of

Z_R and G_R , one obtains the following.

$$\left(\frac{Z_R}{G_R}\right)^{N_2} = \left[\frac{e^{E_{s1}'/RT}}{e^{E_{s2}/RT}}\right]^{N_2} \left(\frac{V_{s1}}{V_{s2}}\right) \quad (7)$$

Then, the natural logarithm form is given by

$$N_2 \ln\left(\frac{Z_R}{G_R}\right) = N_2 \frac{V_{s2}}{V_{s1}} \left(\frac{E_{s1}' - E_{s2}}{RT}\right) \quad (8)$$

$$Z_w = \left\{ \frac{e^{E_{s1}'/RT}}{(1 - e^{-\theta/v_1})^5} \left(1 + n_h e^{-\frac{E_{s1}'}{(x_1-1)RT}}\right) \prod_{i=1}^3 \frac{1}{1 - e^{-\alpha_1 v_i/kT}} \cdot (K)^{\frac{K}{(1+K)^2}} \right\} \left(\frac{V_{s1}}{V_{s2}}\right) \cdot \left\{ \frac{(2\pi m_1 kT)^{3/2}}{h^3} \cdot \frac{eV_1}{N} \cdot \frac{8\pi^2(8\pi^3 I_A I_B I_C)^{1/2} (kT)^{3/2}}{2h^3} \prod_{i=1}^3 \frac{1}{1 - e^{-\alpha_1 v_i/kT}} \right\} \left(\frac{V_{s1} - V_{s2}}{V_{s1}}\right) \quad (9)$$

where $x_1 = \frac{V_1}{V_{s1}}$; E_{s1} is the sublimation energy; θ is the Einstein characteristic temperature; v_i is the internal vibration frequency of the i th mode of a water molecule; n_h is the number of holes next to a molecule; α_1 is a characteristic constant appearing in the significant structure

in which E_{s2} is the sublimation energy of pure hydrocarbon molecule, and E_{s2}' is that of dissolved hydrocarbon molecule in liquid water.

Partition Function for Liquid Water

According to the significant structure theory of liquid water proposed by Jhon, et al. ⁸, the partition function for water is written as follows:

theory, and the other symbols have their usual statistical-mechanical significance.

Considering the effects of orientation on the water surface ⁹, the partition function for the adjacent water next to the hydrocarbon may be written as

$$Z_L = \left\{ \frac{e^{E_{s1}'/RT}}{(1 - e^{-\theta/v_1})^5} \cdot f_R \left(1 + n_h' e^{-\frac{E_{s1}'}{(x-1)RT}}\right) \prod_{i=1}^3 \frac{1}{1 - e^{-\alpha_1 v_i/kT}} (K)^{\frac{K}{(1+K)^2}} \right\} \left(\frac{V_{s1}}{V_{s2}}\right) \cdot \left\{ \frac{(2\pi m_1 kT)^{3/2}}{h^3} \cdot \frac{eV_1}{N} \cdot \frac{8\pi^2(8\pi^3 I_A I_B I_C)^{1/2} (kT)^{3/2}}{2h^3} \cdot \frac{kT}{\mu X} \sin h \frac{\mu X}{kT} \prod_{i=1}^3 \frac{1}{1 - e^{-\alpha_1 v_i/kT}} \right\} \left(\frac{V_{s1} - V_{s2}}{V_{s1}}\right) \quad (10)$$

where

$$f_R = \frac{2\pi(2\pi I_B kT)^{3/2}}{2h} \cdot \frac{kT}{\mu X} \sin h \frac{\mu X}{kT} \quad (11)$$

Then, taking the ratio of the partition func-

tion for pure water molecule, Z_w and that of the adjacent water next to the hydrocarbon molecule, Z_L , one obtains the following equation:

$$\left(\frac{Z_L}{Z_w}\right)^{LN_2} = \frac{\left\{ \frac{e^{E_{s1}'/RT}}{(1 - e^{-\theta/v_1})^5} (1 + n_h' e^{-\frac{E_{s1}'}{(x-1)RT}}) \right\} \left(\frac{V_{s1}}{V_{s2}}\right)^{LN_2} \left\{ \frac{kT}{\mu X} \sin h \frac{\mu X}{kT} \right\} \left(\frac{V_{s1} - V_{s2}}{V_{s1}}\right)^{LN_2}}{\left\{ \frac{e^{E_{s1}'/RT}}{(1 - e^{-\theta/v_1})^5} (1 + n_h e^{-\frac{E_{s1}'}{(x-1)RT}}) \right\} \left(\frac{V_{s1}}{V_{s2}}\right)^{LN_2}} \quad (12)$$

Here, since the ratio of positional degeneracy factor for Z_L and Z_w is quite close to unity, logarithmic ratio becomes zero.

Then, the natural logarithm form is given by

$$LN_2 \ln\left(\frac{Z_L}{Z_w}\right) = LN_2 \frac{V_{s1}}{V_{s2}} \left\{ \frac{E_{s1}' - E_{s1}}{RT} \right.$$

$$\left. + \ln(1 - e^{-\theta/v_1}) + \ln \frac{\pi(2\pi I_B kT)^{3/2}}{h} \right\} + LN_2 \left\{ \ln \frac{kT}{\mu X} \sin h \frac{\mu X}{kT} \right\} \quad (13)$$

Introducing equations (8) and (13) into equation (5), the final equation obtained is as follows:

$$\begin{aligned} \ln Z_D = & N_2 \frac{V_{s2}}{V_2} \left[\frac{E_{s2}' - E_{s2}}{RT} \right] \\ & + LN_2 \frac{V_{s1}}{V_1} \left\{ \frac{E_{s1}' - E_{s1}}{RT} \right. \\ & + \ln(1 - e^{-\epsilon_1/r}) + \ln \frac{\pi(2\pi I_B kT)^{3/2}}{h} \\ & \left. + LN_2 \left\{ \ln \frac{kT}{\mu X} \sin h \frac{\mu X}{kT} \right\} \right. \quad (14) \end{aligned}$$

Then, using this equation (14), the various thermodynamic quantities for the aqueous hydrocarbon solution can be calculated.

Results and Discussion

For the calculations of thermodynamic properties, the parametric values and physical constants in equation(14) must be known.

The parameters used for liquid water in actual calculation are taken from the reference 8. And μX is taken as 18.69×10^{-14} ergs.

The sublimation energy E_{s1}' of the adjacent water next to hydrocarbon molecule is determined as the monolayer approximation for water surfaces, *i. e.*, $E_{s1}' = \frac{9}{12} E_{s1}$. And the sublimation energy E_{s2}' of dissolved hydrocarbon is determined on the basis of experimental values² of free energy and internal energy. The values of $(E_{s2}' - E_{s2})/RT$ used for hydrocarbons are listed and compared with the reference 4,

The number of hydration around a given hydrocarbon molecule are also compared with the reference 2 in Table 1.

And putting the known values for methane¹⁰, benzene¹⁰, ethane¹¹, propane¹¹, butane¹¹, *m*-xylene¹², *p*-xylene¹², toluene¹³, ethylbenzene¹³, and isopropylbenzene¹³, the thermodynamic quantities of aqueous hydrocarbon solutions can be calculated from the following statistical-thermodynamic relationships.

$$\Delta A = -kT \ln Z_D \quad (15)$$

$$\Delta E = kT^2 \left(\frac{\partial \ln Z_D}{\partial T} \right)_V \quad (16)$$

$$\Delta S = - \left(\frac{\partial \Delta A}{\partial T} \right)_V = k \left(\frac{\partial (T \ln Z_D)}{\partial T} \right)_V \quad (17)$$

$$\Delta C_V = \left(\frac{\partial \Delta E}{\partial T} \right)_V = k \left(\frac{\partial}{\partial T} \frac{T^2 \partial \ln Z_D}{\partial T} \right)_V \quad (18)$$

The calculated results are compared with the experimental data in Tables 1 and 2.

In the case of aqueous butane solution, the theoretical curves for Helmholtz free energy change and entropy change of temperature dependence are also compared with the experiments² in Figures 1 and 2.

As shown in the above results, the theory and the experiment are in good agreements.

Table 1. Calculated and observed thermodynamic properties of hydrocarbons in aqueous solution at 298°K

Hydrocarbons	Hydration number		$(E_{s2}' - E_{s2})/RT$		ΔA (kcal/mole)	
	Calc.	Ref. (2)	Calc.	Ref. (4)	Calc.	Obs. (2)
Methane	9.0	13.0	16.88	15.71	2.85	2.51~3.15
Ethane	11.0	16.0	20.59	17.05	3.51	3.32~3.86
Propane	13.0	18.0	23.04	18.26	4.91	4.90~4.91
Butane	15.0	20.0	26.16	19.00	5.92	5.82~6.00
Benzene	18.0	20.0	21.47	...	4.63	4.61
Toluene	19.2	23.0	24.60	...	5.35	5.33
<i>m</i> -Xylene	21.0	25.0	26.20	...	6.11	6.12
<i>p</i> -Xylene	21.3	25.0	26.90	...	6.10	6.11
Ethylbenzene	21.1	26.0	28.34	...	6.07	6.07
Isopropylbenzene	21.5	28.0	29.14	...	6.78	6.76

Table 2. Calculated and observed thermodynamic properties of hydrocarbons in aqueous solution at 298.15 °K

Hydrocarbons	$\Delta E(\text{kcal/mole})$		$\Delta S(e. u.)$		$\Delta C_V(\text{cal/deg}\cdot\text{mole})$	
	Calc.	Obs. ⁽²⁾	Calc.	Obs. ⁽²⁾	Calc.	Ref. ⁽⁴⁾
Methane	-2.04	-2.86~-2.25	-15.3	-18.4~-16.8	8.5	7.1
Ethane	-1.88	-2.37~-1.27	-18.7	-19.5~-16.8	10.3	8.3
Propane	-1.17	-2.09~-1.45	-22.1	-23.5~-21.3	12.2	9.8
Butane	-0.50	-0.96~-0.72	-25.5	-22.7~-21.9	14.1	11.0
Benzene	0.49	0.58	-13.6	-13.5	17.5	...
Toluene	0.58	0.64	-15.8	-15.7	18.8	...
<i>m</i> -Xylene	0.37	0.41	-19.2	-19.1	20.3	...
<i>p</i> -Xylene	0.39	0.46	-18.7	-19.0	20.2	...
Ethylbenzene	0.25	0.39	-19.0	-19.0	20.6	...
Isopropylbenzene	0.93	1.06	-19.7	-19.1	21.0	...

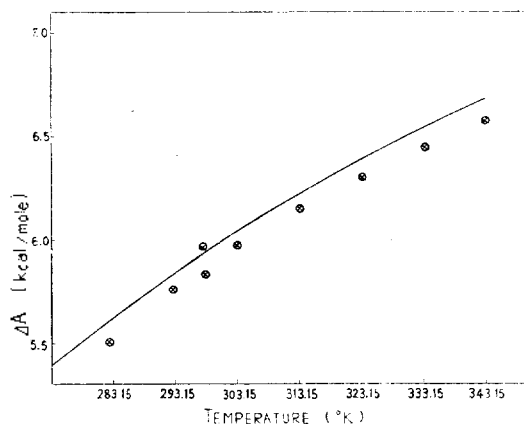


Figure 1. The free energy change of temperature dependence for butane in aqueous solution

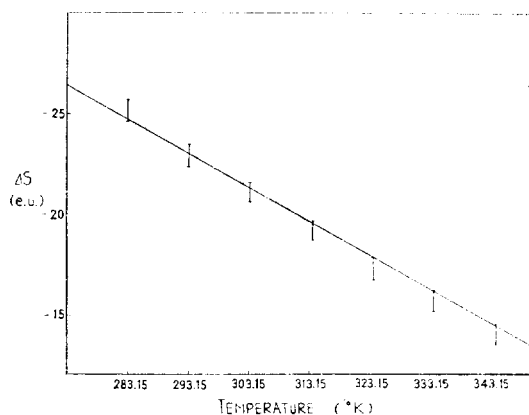


Figure 2. The entropy change of temperature dependence for butane in aqueous solution

If the experimental data of dielectric constants for aqueous hydrocarbon solutions is known, the hydration number of hydrocarbons in Table 1 can be theoretically estimated from the dielectric constant equation of hydration proposed by Sung and Jhon ^{14,15}.

And the potential energy μX is due to the dipole of the water molecule interacting with the effective electric field X .

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